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Contactless monitoring of conductivity changes in vanadium pentoxide xerogel layers using surface acoustic waves

[a]Romualdas Rimeika, [b]Raimundas Sereika, [a]Daumantas Čiplys*, [b,c]Vladimiras Bondarenka, [a]Albertas Sereika, [d]Michael Shur

[a]*Department of Radiophysics, Vilnius University, Saulėtekio 9, Vilnius LT-10222, Lithuania*
[b]*Faculty of Science and Technology, Lithuanian University of Educational Sciences, Studentų 39, Vilnius LT-08106, Lithuania*
[c]*Semiconductor Physics Institute, Center for Physical Sciences and Technology, A. Goštauto 11, Vilnius LT-01108, Lithuania*
[d]*Department of Electrical, Computer, and Systems Engineering and Department of Physics, Applied Physics, and Astronomy, Rensselaer Polytechnic Institute, 110 8th St., Troy, NY 12180-3590, USA*

Abstract

The hydrated form of the vanadium pentoxide ($V_2O_5 \cdot nH_2O$) deposited by the sol-gel method on the piezoelectric YZ-$LiNbO_3$ substrate has been studied using surface acoustic waves (SAWs). Brush-deposited and spin-coated layers, differing in thickness by an order of magnitude (~1 μm and ~0.1 μm, respectively) were studied. The variations with time in the transmitted SAW amplitude and phase during the gel-to-xerogel transition of $V_2O_5 \cdot nH_2O$ were observed and attributed to the acoustoelectric interaction. The possibilities of using the SAWs for contactless monitoring of the layer sheet conductivity have been demonstrated.

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Keywords: vanadium pentoxide; surface acoustic waves; acoustoelectric interaction; thin film conductivity.

1. Introduction

Nanostructured vanadium oxide compounds, and particularly, the hydrated form of vanadium pentoxide ($V_2O_5 \cdot nH_2O$), attract much interest due to their unusual chemical and physical properties and their great potential for applications in chemical industry, for energy storage, various sensors and actuators (Livage 1991, Wang and Cao

* Corresponding author. Tel.: +3705-236-6025; fax: +3705-236-6003.
E-mail address: daumantas.ciplys@ff.vu.lt

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2006). A sol-gel method is a common technique for preparation of $V_2O_5 \cdot nH_2O$ films (Livage et al. 1988), which undergo significant changes during transition from wet gel to xerogel. The recent experiments using surface acoustic waves (SAWs) revealed the strong acoustoelectric interaction in the YZ-$LiNbO_3$ substrate - $V_2O_5 \cdot nH_2O$ layer structures (Sereika at al. 2014, Rimeika et al. 2015). In the present paper, we compare the SAW behaviour during the gel-to-xerogel transition and extract the sheet conductivities of the brush-deposited and spin-coated $V_2O_5 \cdot nH_2O$ layers, the thickness of which differs by an order of magnitude (~1 μm and ~0.1 μm, respectively).

2. Samples and experimental technique

The schematic of experiment is shown in Fig. 1. The SAW interdigital transducers (IDTs) were fabricated on the YZ-$LiNbO_3$ substrates by the standard photolithography. Vanadium pentoxide gels were synthesized using the sol–gel method by dissolving V_2O_5 powder in 10% hydrogen peroxide at room temperature. A drop of gel was spread with a brush in the midway between the IDTs on the free or metalized (with thermally evaporated ~150 nm thick Al film) substrate surface. The typical thickness of as-deposited $V_2O_5 \cdot nH_2O$ layers measured with the profilometer was about 1 μm. Such layers will be further referred to as "thick layers". The layers, further referred to as "thin layers", were obtained by spinning the samples at 2000 RPM for 30 s immediately after the $V_2O_5 \cdot nH_2O$ gel deposition. Their thickness measured by the tapping mode AFM technique was about 0.1 μm.

3. Theoretical background

Due to the acoustoelectric interaction in the conducting film-on-piezoelectric substrate structure, the transmitted SAW amplitude and phase depend on the film sheet conductivity σ_s (see e.g. Ballantine et al. 1997). The changes in amplitude, ΔA, and phase, $\Delta\Phi$, relative to their values at the zero conductivity of the film, respectively are:

$$\Delta A = 8.68\pi \frac{w}{\Lambda} K^2 \frac{\sigma_s/\sigma_m}{1+(\sigma_s/\sigma_m)^2} \qquad \text{(in dB units)} \qquad (1)$$

$$\Delta\Phi = -180 \frac{w}{\Lambda} K^2 \frac{(\sigma_s/\sigma_m)^2}{1+(\sigma_s/\sigma_m)^2} \qquad \text{(in deg units)} \qquad (2)$$

where $\sigma_m = V\varepsilon_0(\varepsilon+1)$, V and Λ are the SAW velocity and wavelength, ε and K^2 are the dielectric constant and squared electromechanical coupling constant of the substrate, respectively, ε_0 is the vacuum permittivity, and w is the film length in the SAW propagation direction. The changes in amplitude and phase normalized to the moduli of their maximum values, $\Delta A/|\Delta A_m|$ and $\Delta\Phi/|\Delta\Phi_m|$, respectively, are plotted in Fig. 2 as the functions of the normalized sheet conductivity of the film. The amplitude minimum is attained at $\sigma_s = \sigma_m$ and the corresponding change is

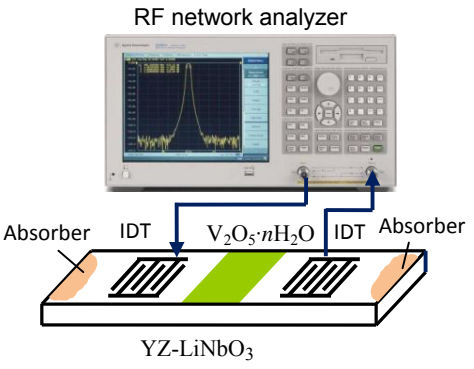

Fig. 1. Schematic of the experimental measurements.

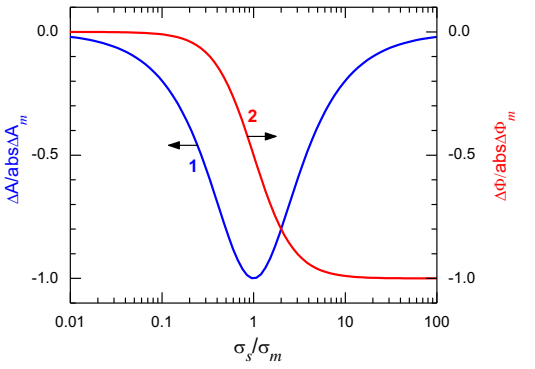

Fig. 2. Theoretical dependencies of transmitted SAW amplitude (1) and phase (2) on film sheet conductivity (in normalized units).

$\Delta A_m = 4.34\pi K^2 w/\Lambda$. When the sheet conductivity of the film varies from zero to infinity, the transmitted SAW phase monotonically decreases, and the corresponding change is $\Delta\Phi_m = -180\,K^2 w/\Lambda$.

The sheet conductivity of the film can be extracted from the amplitude measurements using the expression obtained from (1):

$$\sigma_s = \sigma_m \left[\frac{\Delta A_m}{\Delta A} \pm \sqrt{\left(\frac{\Delta A_m}{\Delta A}\right)^2 - 1} \right]. \tag{3}$$

For each measured ΔA value, one obtains two different values of the sheet conductivity corresponding to the plus and minus signs in (3). For the correct choice, the SAW phase is calculated from (2) using the extracted σ_s values: the calculated phase change must agree with the experimentally measured one.

Experimental results and discussion

The SAW transmission characteristics of the $V_2O_5{\cdot}nH_2O$-on-$LiNbO_3$ structures were investigated as functions of the time passed from the moment of the $V_2O_5{\cdot}nH_2O$ layer deposition. For this purpose, S21 measurements were performed with the radio-frequency (RF) vector network analyzer.

Fig. 3 shows the dependencies of SAW transmission loss on frequency measured at different time moments from the "thick" $V_2O_5{\cdot}nH_2O$ layer deposition on the free substrate surface. As seen, the transmission loss experiences significant variations with time. The similar behaviour was observed for the sample with a „thin" layer on the free substrate surface. In contrast, when the $V_2O_5{\cdot}nH_2O$ layer was deposited on the metalized surface, the SAW transmission was only very slightly affected by "thick" layers and not affected at all by "thin" layers. This is demonstrated by Figures 4 and 5, which show the time dependencies of the SAW transmission loss and phase shift at the IDT center frequency for the both types of $V_2O_5{\cdot}nH_2O$ layers deposited on a free and metalized substrate surface. The strong variations in the transmission loss and phase observed for the free substrate surface and the absence of such variations for the metalized surface are consistent with the acoustoelectric model. As seen from Fig. 5, the loss measured for the "thin" layer on the free surface passes through the maximum, and that for the "thick" layer decreases monotonically with time. The decrease in the transmitted SAW phase with time is observed for the "thin layer" on the free substrate surface, whereas a weaker and more complicated dependence is observed for the "thick layer" on the free surface. On the metalized surface, the SAW phase does not vary with time in the structure with a "thin" layer and only slightly increases with time in the structure with a "thick" layer.

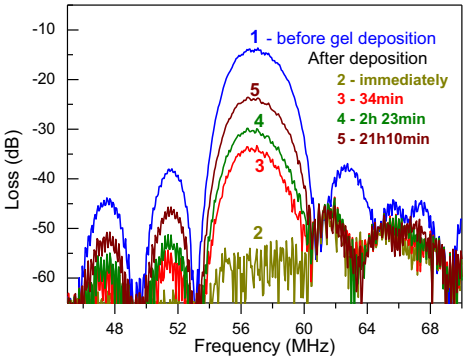

Fig. 3. SAW transmission vs. frequency at different time moments for "thick" $V_2O_5{\cdot}nH_2O$ layer on the free $LiNbO_3$ surface.

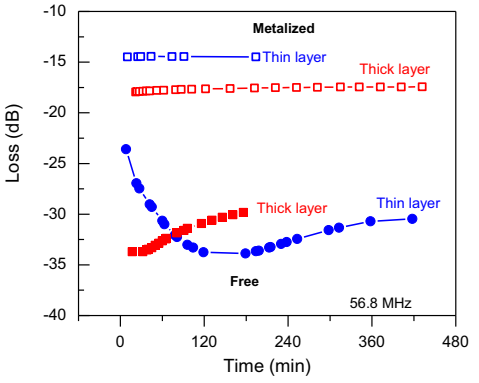

Fig. 4. SAW transmission loss vs. time for "thick" and "thin" layers on free and metrallized substrate surface.

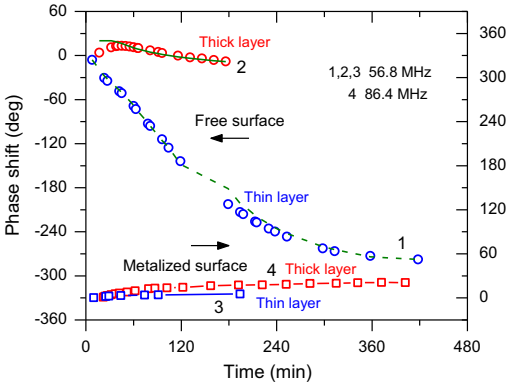

Fig. 5. Transmitted SAW phase vs. time for "thick" and "thin" layers on free and metalized substrate surface. Dots, experiment; lines (1,2) calculated, (3,4) guides for an eye.

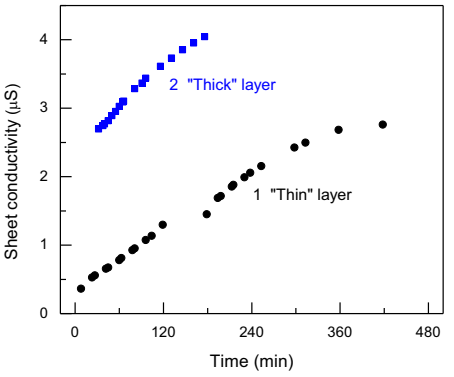

Fig. 6. Sheet conductivities of $V_2O_5 \cdot nH_2O$ layers vs. time from their deposition extracted from the SAW measurements.

Fig. 6 shows the dependencies of sheet conductivities of the $V_2O_5 \cdot nH_2O$ layers on time extracted from the SAW measurements. For the "thin" layer, the change in the SAW amplitude due to the acoustoelectric interaction is defined as the difference between the transmission loss values in the samples with free and metalized substrate surface. The observed decrease in the SAW phase unambiguously implies that the layer sheet conductivity increases with time. The excellent agreement between measured and calculated phase dependencies (curve 1 in Fig. 5) is obtained when the phase values calculated using σ_s values extracted from the amplitude measurements (curve 1 in Fig. 6) are multiplied by the factor 1.5. In the sample with a „thick" layer, the transmitted SAW amplitude only increases with time revealing that the layer sheet conductivities are higher than σ_m , at least starting from 30 min after deposition. Earlier, the amplitude variation is influenced by the liquid gel phase, which is responsible for the dissapearence of transmitted SAW signal and the phase increase in the initial stage of gel-to-xerogel transition. To explain the observed relatively weak variation in the SAW phase, we assume that only a portion of the measured difference between the transmission loss values for the free and metalized substrate surface is due to the acoustoelectric interaction. The sheet conductivity dependence is extracted using (3) from this portion and shown by curve 2 in Fig. 6. The remaining loss is assumed to be constant and its value is determined from the best fit of the measured and calculated dependencies of the SAW phase (curve 2 in Fig. 5).

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